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- (54) Stabilized Halogen-Containing Resin Composition
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SPECIFICATION

TITLE OF THE INVENTION
Stabilized Halogen-Containing Resin Composition

What is claimed is:

1. A stabilized halogen-containing resin composition which is composed by adding (i) an organic acid metal salt, (ii) a basic metal salt and (iii) an isocyanurate compound represented by the following general formula [I] to a halogen-containing resin.

In the above formula, R1, R2 and R3 represent -CH2OH, CH2CH2OH, -CH2CH2COOH,

- 2. The stabilized halogen-containing resin composition of Claim 1, wherein the organic acid metal salt is a metal salt of carboxylic acids.
- 3. The stabilized halogen-containing resin composition of Claim 1, wherein the organic acid metal salt is a metal salt of phenols.
- 4. The stabilized halogen-containing resin composition of Claim 1, wherein the basic metal salt is a basic inorganic acid metal salt.

- 5. The stabilized halogen-containing resin composition of Claim 1, wherein the basic metal salt is a basic organic acid metal salt.
- 6. The stabilized halogen-containing resin composition of one of Claims 1 to 5, wherein the metal salt is chosen from metal salts of Li, Na, K, Mg, Ca, Ba, Sr, Zn, Ti, Al, Zr and Sn.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a stabilized halogencontaining resin composition.

More particularly, the present invention relates to a stabilized halogen-containing resin composition which is stabilized by adding an organic acid metal salt, a basic metal salt and an isocyanurate compound to a halogen-containing resin.

Generally, halogen containing resins are low in thermostability and light stability, and heat decomposition can easily occur in heat molding processes mainly due to dehydrohalogenation. This can result in degraded mechanical properties and unwanted changes in color of the processed products thereof, which are notable disadvantages.

To avoid the above disadvantages, one or more heat stabilizers can be added to the plastic resin to suppress the deterioration thereof in the production process.

A number of metallic soaps is used for this purpose and almost satisfactory results are obtained in terms of thermostability.

However, use of metallic soaps, especially cadmium soaps and lead soaps, causes a major problem relating to toxicity.

To avoid the above problem, a combination of soaps

except for cadmium soap and lead soap, or nonmetal stabilizers are used and a certain level of thermostability has been obtained.

However, the thermostability is still inferior in comparison with cadmium soap or lead soap, and other drawbacks are introduced. Thus, the above solutions fail to satisfy the technical requirements as a stabilizer.

For example, the combination of calcium, zinc, magnesium or barium soap and polyhydric alcohol, diphenylthiourea or tris nonylphenyl phosphite cannot provide sufficient stabilizing effect and is not suitable for practical use.

Also, the combination of the above metallic soaps and phenylindole brings a certain level of stabilizing effect, but promotes photo-deterioration.

Even more particularly, aminocrotonic ester has a very low compatibility with halogen containing resins, and does not have a sufficient effect especially on a polyvinyl chloride obtained by suspension polymerization.

On the other hand, especially for processed products used for food packing, a variety of prescriptions for non-toxic stabilizers has been conceived and, as a result of their desirable properties, have been widely applied to food packing materials. However, the field of application is still very much confined.

Recently, with progress in the processing technology of halogen containing resins, a number of food packaging materials and food containers have appeared commercialy. At the same time, there is increasing demand for an excellent non-toxic stabilizer preventing heat decomposition in high temperature molding processes and which can endure severe operating conditions during the whole process of various molding methods.

In order to meet the above demands, a low-toxic stabilizer of the dioctyltin family has been conceived and put to practical use, however, long term workability in the molding process required improvement.

Properties required for a non-toxic stabilizer in food packing material molding include sufficient stabilizing effect with a small amount of stabilizer, a high compatibility with resins and low migration characteristics.

In calender roll processing, for example, plateouts can occurs on the surface of the calender roll and damage the surface of a molded product. This results in decreased efficiency in processing.

The plateout mentioned above, which can also occur also in processing methods other than calender roll processing, is a drawback in stabilizing the halogen containing resins using metallic soaps.

In view of the above circumstances, the inventors found, as a result of long years of research, a halogen-containing resin composition which has excellent stability with respect to photo-deterioration and heat deterioration, and accomplished the present invention.

More specifically, the present invention provides a stabilized halogen-containing resin composition which is composed by adding (i) an organic acid metal salt, (ii) a basic metal salt and (iii) an isocyanurate compound represented by the following general formula [I], to a halogen-containing resin.

In the above formula, R1, R2 and R3 represent -CH2OH, CH2CH2OH, -CH2CH2COOH,

-CH
$$_2$$
-CH-CH $_2$, -CH2-CH=CH2 or -CH $_2$ -CH-CH $_2$. . . OH OH

Hereinafter, the present invention is explained in greater detail. The organic acid metal salt is a metal salt of a carboxylic acid or a phenol. Examples of the carboxylic acid include caproic acid, pelargonic acid, lauric acid, 2-ethylhexyl acid, myristic acid, cetylic acid, undecylenic acid, ricinoleic acid, linolic acid, linoleic acid, neo acid, oleic acid, stearic acid, isodecanoic acid, isostearic acid, 12-hydroxystearic acid, 12-ketostearic acid, chlorostearic acid, phenylstearic acid, arachic acid, behenic acid, erucic acid, brassidic acid and mixture of naturally produced acids such as tallow fatty acid, coconut oil fatty acid, china wood oil fatty acid, bean oil fatty acid and cotton-seed oil fatty acid, benzoic acid, chlorobenzoic acid, toluic acid, ortho-hydroxybenzoic acid, p-t-butyl benzoic acid, 5-t-octyl ortho-hydroxybenzoic acid, naphthenic acid, xylic acid, ethylbenzoic acid, isopropyl benzoic acid, di-t-butyl benzoic acid, bromobenzoic acid, monobutyl malate, monodecyl phthalate and cyclohexane carboxylic acid.

And, for phenols, carbolic acid and alkylphenol are preferred, which include creosol, ethylphenol, dimethylphenol, isopropylphenol, cyclohexyl phenol, t-butylphenol, 2-hydroxybiphenyl, nonylphenol, dinonylphenol, methyl t-butylphenol, tetra methylphenol, poly (di-penta) isopropylphenol, diisopropyl-m-cresol, butylphenol, isoamyl phenol, isooctylphenol, 2-ethylhexyl phenol, t-nonylphenol, decyl phenol, t-dodecylphenol, t-octyl phenol, octyl phenol, an isohexyl phenol, an octadecyl phenol, diisobutyl phenol, a methylpropyl phenol, methyl-t-octyl phenol, di-t-nonylphenol and di-t-dodecylphenol.

A preferred metal composition of the metal salt includes Zn, Ba, Ca, Sn, Mg, Sr and the like.

0.01 to 10, preferably 0.1 to 3 parts by weight of the organic acid metal salt should be added with respect to 100 parts by weight of the resin.

The basic metal salt is a basic inorganic acid metal

salt or an organic acid metal salt, in which the preferred metal composition is Li, Na, K, Mg, Ca, Sr, Ba, Zn, Ti, Al, Zr, Sn or the like, and the preferred inorganic acid includes phosphoric acid, phosphorous acid, silicic acid, nitric acid, nitrous acid, sulfuric acid, sulfur dioxide, boric acid and the like.

The inorganic acid salt of the present invention can be synthesized from the inorganic acid and, the metal, the chloride thereof, the oxidate thereof or the ammonium salt thereof through a reaction such as coprecipitation or fusion, according to the usual methods.

The aforementioned salts may take the form of double salts, and can be an anhydride or have combined water.

Moreover, the salts may be an arbitrary mixture of the inorganic acid normal salt and a chloride, a hydroxide or an oxidate.

Examples of the preferred basic inorganic acid salt include 3CaO.Na₃PO₄, 5CaO.NaHPO₄, MgO.Mg₃(PO₄)₂, 3CaO.Ca₃(PO₄)₂, Ca(OH)₂.Ca₃(PO₄)₂, Ba(OH)₂.Ca₃(PO₄)₂.3H₂O, $Sr(OH)_2.Sr_3(PO_4)_2$, $BaO.Ba_3(PO_4)_2$, $3Ba(OH)_2.Ba_3(PO_4)_2$, $ZnO.Zn_3(PO_4)_2$, $2ZnO.Ba_3(PO_4)_2$, $Al_2O_3.AlPO_4$, $3SnO.Sn_3(PO_4)_2$, Ba(OH)₂.NaHPHO₃, 5CaO.NaHPHO₃, 3Ba(OH)₂.K₂PHO₃, MgO.MgPHO₃, $5Mg(OH)_2.MgPHO_3$, CaO.CaPHO₃, $3Ca(OH)_2CaPHO_3$, $Ba(OH)_2.CaPHO_3$, 5CaO.CaPHO3, BaO.BaPHO3, 2Ba(OH)2.BaPHO3. 3Ba(OH)₂.BaPHO_{3.3}H₂O, ZnO.ZnPIO₃, ZnO.3CaPHO₃, TiO₂.Ti(PHO₃)₂, Al₂O₃.Al₂(PHO₃)₃, 3ZrO.ZrPHO₃, SnO.SnPHO₃, 3SnO.SnPHO₃, $Mg(OH)_2.Mg_2SiO_4$, $3MgO.MgSiO_3$, $MgO.K_2SiO_3$, $CaO.Ca_2SiO_4$, 3CaO.Li₂SiO₃, 3CaO.CaSi₂O₅, 2Ca(OH)₂.Ca₂Si₃O₈, SrO.SrSiO₃, 5BaO.Ba₂SiO₄, Ba(OH)₂.Ba₂SiO₄.6H₂O, Ba(OH)₂.BaSiO₃, 3Ba(OH).BaSi₂O₅, 3BaO.Ba₂SiO₄, Ba(OH)₂.CaSiO₃, 2ZnO.ZnSiO₃, $ZnO.3CaSiO_3$, $CaO.Sn_2SiO_4$, $Mg(OH).Mg(NO_3)_2$, $3CaO.Ca(NO_3)_2$, 2Ca(OH)₂.Ca(NO₂)₂.5H₂O, 3BaO.Ba(NO₃)₂, Ba(OH)₂.Na₂SO₄, $ZnO.K_2SO_4$, $3CaO.K_2SO_3$, $Mg(OH)_2.MgSO_4$, $5MgO.MgSO_3$, $2MgO.MgSO_3$, MgO.CaSO₃, 5CaO.CaSO₄, Ca(OH)₂.CaSO₄, 3CaO.CaSO₃, SrO.SrSO₂, $3BaO.BaSO_4$, $3BaO.CaSO_3$, $Ba(OH)_2.BaSO_4$, $TiO_2.Ti(SO_4)_2$, $Al_2O_3.Al_2(SO_4)_3$, $Al(OH)_2.MgSO_4$, $MgO.Mg_3(BO_4)_2$, $CaO.Ca_3(BO_4)_2$,

 $5Ca (OH)_2 \cdot Ca_3 (BO_4)_2$, $3CaO \cdot Ca (BO_2)_2$, $3Ba (OH)_2 \cdot Ba_3 (BO_4)_2$, $3BaO \cdot BaB_4H_7$ and $5Ba (OH)_2 \cdot Ba (BO_2)_2$.

Furthermore, the basic inorganic acid salt of the present invention can be a compound in which one of the above metals is bonded with only hydroxy group or oxygen, namely a hydroxide such as $Mg(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$ and $Ba(OH)_2$, or an oxidate such as MgO, CaO, BaO, Al_2O_3 and SnO_2 .

Also, the basic organic salt is an essentially stable product obtained through a publicly known method in which organic acids such as carboxylic acids, sulfonic acid, organic phosphoric acids or phenols and a stoichiometrically excessive amount of metal, or chloride, oxidate or hydroxide thereof are reacted, and is called a hypersaline, superbasic or a basic complex.

As for the basic organic salt of the present invention, the excessive amount of above compounds includes up to about 30 times the equivalent amount thereof.

And, the basic organic salt of the present invention includes a metallic carboxylate, an arbitrary mixture of a metal phenolate and a metal oxide or a metal hydroxide, and a basic organic salt of which the basicity is reduced through a process using an acid gas such as carbon dioxide.

0.01 to 10, preferably 0.1 to 3 parts by weight of the basic metal salt should be added with respect to 100 parts by weight of a resin.

Examples of the preferred isocyanurate compound represented by the general formula [I] include tris (hydroxyethyl) isocyanurate, tris (glycidyl) isocyanurate, triallyl isocyanurate, tris (carboxyethyl) isocyanurate, tris (hydroxymethyl) isocyanurate, tris (dihydroxypropyl) isocyanurate, diglycidyl allyl isocyanurate, monoglycidyl diallyl isocyanurate, monoglycidyl bis (dihydroxypropyl) isocyanurate, diglycidyl dihydroxypropyl isocyanurate, allyl glycidyl dihydroxypropyl isocyanurate and the like.

0.01 to 10, preferably 0.1 to 3 parts by weight of the isocyanurate compound should be added with respect to 100

parts by weight of the resin.

Epoxides that can be used with the present invention include epoxidized soybean oil, epoxidized linseed oil, epoxidized fish oil, epoxidized tall oil fatty acid ester, epoxidized beef tallow oil, epoxidized polybutadiene, epoxidized methyl stearate, epoxidized butyl stearate, epoxidized 2 ethylhexyl stearate, epoxidized stearyl stearate, epoxidized castor oil, epoxidized safflower oil, epoxidized linseed oil fatty acid butyl, 3-(2-xenoxy)-1,2-epoxypropane, bisphenol-A diglycidyl ether, vinylcyclohexene diepoxide, dicyclopentadiene diepoxide, 3,4- epoxy cyclohexyl-6-methyl epoxycyclohexane carboxylate and the like.

0.01 to 10, preferably 0.1 to 5 parts by weight of the above epoxides should be added with respect to 100 parts by weight of a resin.

Organic phosphite compounds that can be used with the present invention include diphenyl decyl phosphite, triphenyl phosphite, tris-nonylphenyl phosphite, tridecyl phosphite, tris (2-ethylhexyl) phosphite, tributyl phosphite, dilauryl acid phosphite, dibutyl acid phosphite, tris (dinonyl phenyl) phosphite, trilauryl trithio phosphite, trilauryl phosphite, bis (neopentyl glycol)-1,4cyclohexane dimethyl phosphite, distearyl pentaerythritol diphosphite, diisodecyl pentaerythritol diphosphite, diphenyl acid phosphite, tris (lauryl-2-thioethyl) phosphite, tetra tridecyl-1,1,3-tris (2'-methyl-5'-tertiary butyl-4'-oxyphenyl) butane diphosphite, tetra (C12 - C15 mixed alkyl) 4,4'-isopropylidene diphenyl diphosphite, tris (4-oxy-2,5-di-tertiary butylphenyl) phosphite, tris (4-oxy-3,5-di-tertiary butylphenyl) phosphite, 2-ethylhexyl diphenyl phosphite, tris (mono-/di-mixed nonylphenyl) phosphite, hydrogenated-4,4'-isopropylidene diphenol polyphosphite, diphenyl bis [4,4-n-butylidene bis (2tertiary butyl-5-methylphenol)] thiodiethanol diphosphite, bis (octylphenyl).bis (4,4'-n-butylidene bis (2-tertiary

butyl-5-methylphenol)]-1,6-hexanediol diphosphite, phenyl-4,4'-isopropylidene diphenol.pentaerythritol diphosphite, phenyldiisodecyl phosphite, tetratridecyl-4.4'-n-butylidene bis (2-tertiary butyl-5-methylphenol) diphosphite, tris (2,4-di-tertiary butylphenyl) phosphite and the like.

0.01 to 10, preferably 0.1 to 5 parts by weight of the above organic phosphite compounds should be added with respect to 100 parts by weight of a resin.

As for the polymer composition of the present invention, a phthalate or other ester plasticizers, a polyester plasticizer, a phosphate plasticizer, an epoxy plasticizer, a chloride plasticizer and other plasticizers can be used appropriately.

Addition of an antioxidant to the polymer composition of the present invention can increase resistance of the said polymer composition to oxidation degradation and can be employed appropriately.

The above antioxidant includes a phenolic antioxidant, a sulfur compound and the like.

An ultraviolet absorber added to the polymer composition of the present invention can increase photostability and can be selected and employed appropriately.

The above ultraviolet absorber can be benzophenone based, benzotriazole based, salicylate based, substituted acrylonitrile based, various metal salts or metal chelates, especially nickel or chromic salt or nickel or chromic chelate, triazine based, and the like.

Even more particularly, to obtain a non-toxic and highly thermostable halogen-containing polymer composition, a non-toxic metallic soap should be chosen among the above metallic soaps that are usually used.

In addition, the composition can include, for example, pigments, bulking agents, blister agents, antistatic agents, anti-fogging agents, plateout inhibitors, finishing agents, lubricants, fire proofing agents, fluorescence agents,

fungicides, antibacterials, metal deactivators, photodeterioration inhibitors, infrared radiation absorbers, sulfate esters, thiourea derivatives, processing aids, parting agents, reinforcers and the like as necessary.

Halogen containing polymers that can be used with the present invention include, for example, halogen containing plastic resins such as polyvinyl chloride, polyvinyl bromide, polyvinyl fluoride, polyvinylidene chloride, chlorinated polyethylene, chlorinated polypropylene, brominated polyethylene, chlorinated rubber, vinylchloridevinylacetate copolymer, vinylchloride-ethylene copolymer, vinylchloride-styrene copolymer, vinylchloride-isobutylene copolymer, vinylchloride-vinylidenechloride copolymer, vinylchloride-styrene-maleic anhydride terpolymer, vinylchloride-styrene- acrylonitrile copolymer, vinylchloride-butadiene copolymer, vinylchloride-isoprene copolymer, vinylchloride-vinylidenechloride-vinylacetate terpolymer, vinylcholoride-acrylicester copolymer, vinylchloride-maleicester copolymer, vinylchloridemethacrylicester copolymer, vinylchloride-acrylonitrile copolymer, a halogen-containing plastic resin such as internal plasticizing polyvinylchloride, and a blended material of aforementioned halogen-containing plastic resin with an alpha olefin polymer in which the alpha olefin is selected from the group of polyethylene, polypropylene, poly-3-methylbutene, or ethylene-vinyl acetate copolymer, polyolefins such as ethylene-propylene copolymer and copolymers of the polyolefins, copolymer of polystyrene, acrylic resin or styrene with another monomer (e.g., maleic anhydride, butadiene, acrylonitrile and the like), acrylonitrile-butadiene-styrene copolymer, acrylic esterbutadiene-styrene copolymer, and methacrylic esterbutadiene-styrene copolymer.

The examples shown hereinafter represent the effect of halogen containing polymer composition of the present

invention; however, the present invention is not limited by the examples.

EXAMPLE 1

In order to demonstrate the effect of the present invention, the compositions having following formulations were subjected to a kneading roll process to produce a sheet having a thickness of 1 millimeter. The sheet was subjected to a thermal aging test at 180 °C, initial tinting test and transparency test.

The results are shown in Table 1.

polyvinyl chloride resin	100 parts by weight
Dioctylphthalate	50
Epoxidized soybean oil	3.0
Calcic stearate	1.0
Zinc stearate	0.5
Ca ₃ (PO4) ₂ .3Ca (OH) ₂	0.5
Isocyanurate compound (Table 1)	0.1

Table 1

	Sample	Thermostability	Initial	Transparency
		(min)	tinting	
Comparative	Not Added	45	Bad	Satisfactory
Example 1-1				
Comparative	Penta erythritol	55	Satisfacto	Bad
Example 1-2			ry	
Comparative	Sorbitol	50	Slightly	Bad
Example 1-3			Bad	
Example 1-1	Tris	65	Very Good	Very Good
	(hydroxyethyl)			
	isocyanurate			
Example 1-2	Triallyl	65	Very Good	Good
	isocyanurate			
Example 1-3	Tris	60	Very Good	Very Good

	(hydroxymethyl) isocyanurate			
Example 1-4	Tris (glycidyl) isocyanurate	65	Very Good	Very Good
Example 1-5	Diglycidyl allyl isocyanurate	65	Very Good	Good
Example 1-6	Tris (carboxyethyl) isocyanurate	60	Very Good	Good

EXAMPLE 2

In order to demonstrate the effect of the present invention, the compositions having the following formulations were subjected to a thermostability test at 190°C, initial tinting test and plateout performance test. The results are shown in Table 2. Note that the plateout value indicates ppm value of pigment plated out under the "Watching Red" Method.

The results are shown in Table 2.

Polyvinyl chloride resin	100 parts by weight
Epoxidized soybean oil	3
Zinc stearate	0.5
Benzoic acid calcium	0.5
Magnesium stearate	0.5
Tris (hydroxyethyl) isocyanurate	0.5
Basic metal salt (Table 2)	1.0

Table 2

	Basic metal salt	Thermostability (min)	Initial tinting	Plateout performance
Comparative Example 2-1	Not Added	70	Bad	(ppm) 210

Comparative	Ca ₃ (PO ₄) ₂	60	Slightly	300
Example 2-2			Good	
Example 2-1	Ca ₃ (PO ₄) ₂ .3Ca (OH) ₂	95	Very	80
			Good	
Example 2-2	Mg ₃ (PO ₄) ₂ .3MgO	95	Very	85
			Good	
Example 2-3	Zn ₃ (PO ₄) ₂ .ZnO	95	Very	80
			Good	
Example 2-4	Ca ₂ SiO ₄ .3CaO	90	Very	80
			Good	
Example 2-5	CaSiO3.CaO	95	Good	90
Example 2-6	BaSiO ₃ .3BaO	90	Good	90
Example 2-7	CaHPO ₃ .5Ca (OH) ₂	90	Very	80
			Good	ļ
Example 2-8	Ba ₃ (PO ₄) .5BaO	95	Good	80
Example 2-9	Ca ₃ (PO ₄) ₂ one part	95	Very	85
	Ca(OH)2 one part		Good	
Example 2-	Ca ₂ SiO ₄ one part	95	Very	85
10	Ca(OH) ₂ five part		Good	
Example 2-	Mg0	80	Slightly	110
11			Good	
Example 2-	Calcium	95	Very	80
12	petronateHMW*1		Good	

*1 Hyperbasic calcium sulfonate chelate manufactured by Witco Chemical Co.(US)

EXAMPLE 3

In order to demonstrate the effect of using Zn salt - Ba salt, the compositions having following formulations were subjected to the tests conducted according to the procedure of Example 1.

The results are shown in Table 3.

Polyvinyl chloride resin	100 parts by weight
Epoxidized soybean oil	5
Toluic acid zinc	0.5
Nonylphenol barium salt	1.5
Stearic acid	1.0
Ca ₂ SiO ₂ .8Ca (OH) ₂	1.0
Isocyanurate compound (Table 3)	0.3

Table 3

Example	Additive	Thermostability	Initial	Transparency
		(at 190°C)	tinting	
Comparative	Not Added	60 min	Good	Good
Example 3-1				
Comparative	Mannitol	65	Slightly	Slightly Good
Example 3-2			Good	
Comparative	Trimethylolpropan	70	Good	Good
Example 3-3	е			
Example 3-1	Tris	95	Excellent	Very Good
	(hydroxyethyl)			
	isocyanurate			
Example 3-2	Tris (glycidyl)	90	Very Good	Very Good
	isocyanurate			
Example 3-3	Triallyl	85	Very Good	Good
	isocyanurate			
Example 3-4	Tris	85	Very Good	Good
	(dihydroxypropyl)			
	isocyanurate			

EXAMPLE 4

In order to demonstrate the effect of the polymer blend including polyvinyl chloride resin and ABS resin, the compositions having following formulations were subjected to the tests conducted according to the procedure of Example 1.

The results are shown in Table 4.

<Formulation>

Polyvinyl chloride resin 80 parts by weight ABS resin 20

Epoxidized soybean oil 5

Ba - Zn octoate liquid stabilizer 2

Stearic acid 0.5

Tetra (C12 - C15 mixed alkyl)

bispenol A diphosphite 0.2

Tris (glycidyl) isocyanurate 0.1

Basic metal salt (Table 4) 0.2

Table 4

		т	
Example	Basic metal salt	Thermostability	Initial
		(at 190°C)	tinting
Comparative	Not Added	100 min	Satisfactory
Example 4-1			
Example 4-1	CaSiO ₄ .3CaO	120	Very Good
Example 4-2	BaSO ₄ .5Ba(OH) ₂	110	Very Good
Example 4-3	Al ₂ (SO ₄) ₃ .Al ₂ O ₃	120	Very Good
Example 4-4	Ca (OH) ₂	105	Good
Example 4-5	Ba (NO ₂) ₂ .5BaO	120	Very Good
Example 4-6	Ba ₃ (PO ₄) ₂ One part	120	Very Good
	Ba(OH) ₂ Five parts		
Example 4-7	Ca(PO ₄) ₂ .5Ca (OH) ₂	120	Very Good
Example 4-8	Ba ₃ (PO ₄) ₂ .8BaO	110	Very Good
Example 4-9	MgSiO ₃ .3MgO	110	Very Good
Example 4-	LD-2105 *1	120	Very Good
10			
Example 4-	LD-2106 *2	120	Very Good
11			
Example 4-	LD-2110 *3	120	Very Good
12			

^{*1} Hyperbasic calcium phenate manufactured by The Lubrizol Corporation (US)

 $[\]ensuremath{^{\star2}}$ Hyperbasic barium phenate manufactured by the same corporation

 $\ensuremath{^{\star3}}$ Hyperbasic calcium sulfonate manufactured by the same corporation

EXAMPLE 5

In order to demonstrate the effect of the organic phosphite compound, the compositions having following formulations were subjected to the tests conducted according to the procedure of Example 1.

The results are shown in Table 5.

Polyvinyl chloride resin	100 parts by
	weight
Calcic stearate	1.0
Zinc instearate	0.5
Organic phosphite compound (Table 5)	0.3
$CaSO_4.5Ca(OH)_2.1/2H_2O$	2.0
Tris (hydroxyethyl) isocyanurate	0.8

Table 5

	Organic phosphite	Thermostability	Initial
	compound	(at 190°C)	tinting
Example	Not Added	80	Satisfactory
5-1			
Example	Tris nonylphenyl	-	Good
5-2	phosphite		
Example	Diphenyl-2-ethylhexyl	105	Very Good
5-3	phosphite		
Example	Dibisphenol A-isodecyl	120	Very Good
5-4	phosphite		
Example	Diphenylisodecyl	115	Very Good
5-5	phosphite		
Example	Phenyl-bisphenol A-	115	Very Good
5-6	pentaerythritol		
	diphosphite		

Example	Tetra (tridecyl) bispenol	120	Very Good
5-7	A-diphosphite		

EXAMPLE 6

In order to demonstrate the synergic effect of the addition of other additives to the composition of the present invention, the compositions having following formulations were subjected to the tests conducted according to the procedure of Example 1.

The results are shown in Table 6.

<Formulation>

Polyvinyl chloride resin

(vinyl chloride 95%, vinyl acetate 5%)	100 parts by
	weight
12-OH-barium stearate	2.0
Zinc stearate	0.5
Tris (hydroxyethyl) isocyanurate	0.5
Other additives (Table 6)	0.1
$Ca_3(PO_4)_2$	0.5
Ca (OH) 2	0.5

Table 6

Example	Additive	Thermostabi	Initial	Penetrability
		lity	tinting	
		(at 190°C)		
Example	Not Added	75 min	Very Good	Good
6-1				
Example	2,6-di-t-butyl-p-	90	Very Good	Good
6-2	cresol			
Example	Nitrilotriacetic	105	Very Good	Very Good
6-3	acid tributyl]	
	amide	1		
Example	Sorbic acid	90	Very Good	Very Good
6-4				

Example 6-5	Diphenylthiourea	85	Very Good	Good
Example 6-6	Phenylindole	100	Very Good	Very Good
Example 6-7	Thiodipropionic acid	100	Very Good	Very Good
Example 6-8	Dilauryl thiodipropionate	105	Very Good	Good
Example 6-9	Thiodiethanol bis	110	Very Good	Good
Example 6-10	Bisphenol A	90	Very Good	Very Good